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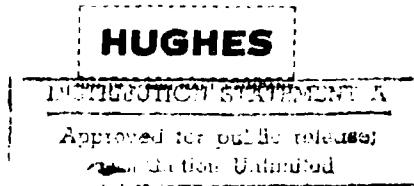
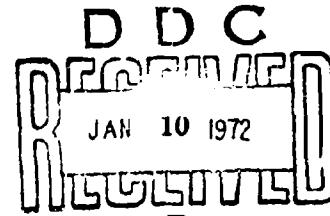
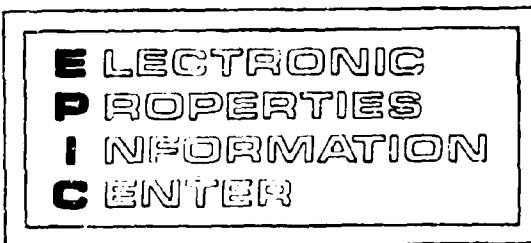
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**DATA COMPILATION ON  
VANADIUM OXIDES**

**M. NEUBERGER**

**NOVEMBER 1971**

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## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Hughes Aircraft Company Culver City, California 90230		2a. REPORT SECURITY CLASSIFICATION Unclassified
2b. GROUP		
3. REPORT TITLE Data Compilation on Vanadium Oxides		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Interim Report		
5. AUTHOR(S) (First name, middle initial, last name) M. Neuberger		
6. REPORT DATE November 1971	7a. TOTAL NO. OF PAGES 61	7b. NO. OF REFS 116
8a. CONTRACT OR GRANT NO. DSA 900-72-C-1182	8b. ORIGINATOR'S REPORT NUMBER(S) EPIC-IR-79	
b. PROJECT NO.		
c.		
d.		
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited		
11. SUPPLEMENTARY NOTES Copies are available from NTIS for \$6.00 each.	12. SPONSORING MILITARY ACTIVITY U.S. Defense Supply Agency Defense Electronics Supply Center Dayton, Ohio	
13. ABSTRACT  The change in crystal structure at the transition temperature in several of the vanadium oxides, causes a drastic change in resistivity as the material is heated (or cooled). This phenomenon is being applied to the manufacture of a number of devices.  All available information on the crystal structure, physical, mechanical, thermal, optical, magnetic and electronic properties of bulk and film samples, has been tabulated in this compilation. Graphs illustrating these features are included.		

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Vanadium Oxides Transition Metal Oxides Electrical Properties Optical Properties Magnetic Properties Thermal Properties Mechanical Properties Crystallographic Properties Phase Diagrams Electronic Switching Devices						

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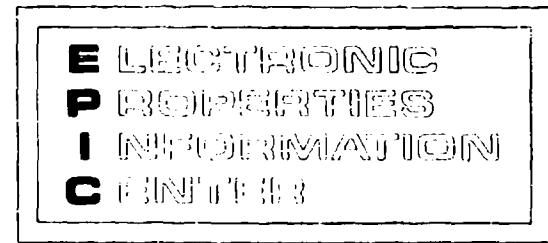
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ACKNOWLEDGEMENT

The Electronic Properties Information Center is operated by Hughes Aircraft Company under contract to the U.S. Defense Supply Agency (DSA 900-72-C-1182); technical aspects of EPIC operations are monitored by the Air Force Materials Laboratory. The support of these sponsor organizations is gratefully acknowledged.

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Library of Congress Catalog Card Number: 75-18578

## ABSTRACT

The change in crystal structure at the transition temperature in several of the vanadium oxides, causes a drastic change in resistivity as the material is heated (or cooled). This phenomenon is being applied to the manufacture of a number of devices.

All available information on the crystal structure, physical, mechanical, thermal, optical, magnetic and electronic properties of bulk and film samples, has been tabulated in this compilation. Graphs illustrating these features are included.

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## INTRODUCTION

Several vanadium oxides,  $V_0_{0.8-1.3}$ ,  $V_2O_3$  and an entire series of non-stoichiometric vanadium oxides, show a crystallographic transformation from a low to high temperature phase. According to Hyland,\* there is no extensive rearrangement of the atoms, only slight distortions of the original atomic grouping which is rapidly reversible at the transition temperature. Fillingham in an optical study of the domain structure in  $V_2O_3$ , indicates that displacement of the atom positions is small and comprises only slight distortions of the  $VO_6$ -octahedra chains as vanadium atom doublets form, alternately nearer to and farther from one another in the low temperature (monoclinic) phase. As the crystal moves through the transition temperature, domain patterns show only in the monoclinic phase, there are no domains evident in the tetragonal phase.

These alternating long and short separations of the cations along the  $a$ -axis ( $2.65\text{\AA}$  and  $3.12\text{\AA}$ ) shift above the transition temperature and the cations form a body-centered tetragonal array;  $V-V = 2.87\text{\AA}$  along the  $c$ -axis. As a result,  $a_{\text{monoclinic}} = 2c_{\text{tetragonal}}$  and  $Z=2$  becomes  $Z=4$ .

This shift in crystal structure must evidently exercise a strong effect on the electronic properties of the several vanadium oxides and, consequently, on the band structure. The most marked and useful change is a rise in conductivity as the vanadium dioxide is heated through its transition temperature of  $68^\circ\text{C}$  where the material passes from a semiconducting to a metallic state. The conductivity is 5 orders of magnitude in  $V_2O_3$  and 9 orders of magnitude in  $V_2O_3$ . The shift is also anisotropic and, depending on the sample quality, may also exhibit hysteresis.

Single crystals in the series  $V_nO_{2n-x}$  with  $x$  equal to an integer, have been studied by Okinaka et al., Kosuge and Nagasawa. Transition temperatures in this series vary from  $68^\circ\text{C}$  to  $-140^\circ\text{C}$ . The composition  $V_5O_9$  has a resistivity jump on cooling through  $125^\circ\text{K}$  of  $\sim 10^7 \Omega\text{cm}$  and together with  $V_6O_{11}$  shows an increase in thermal emf at the transition temperature from  $-10$  to  $-800 \mu\text{V}/^\circ\text{K}$ .

\* All references are listed alphabetically by name, in the bibliography at the end of this report.

This change in the several properties of the vanadium oxides is being applied to the manufacture of a variety of switching and modulation devices, since the time constant is about 20 nanoseconds. (Schmidt, Cope & Penn, Walden, Kennedy & Collins; Van Steense).

Other electronic and physical properties also show a discontinuity at the transition temperature; magnetic susceptibility, thermoelectric power, specific heat, thermal expansion, reflectivity and transmission spectra. Graphs illustrating these features are included.

Band structures have been formulated, based in general on the theoretical considerations of Goodenough, by many experimentalists. These include Hyland, Verleur et al., Bongers, Powell et al., Berglund & Guggenheim, Austin & Turner, Mokerov & Rakov and Adler. Austin & Mott, in a recent discussion of the transition metal oxides, ascribe their properties to Coulomb interactions between the d-electrons and a strong electron-lattice coupling. With others in this field, they also agree that disorder and defects have a marked influence in leading to localized electron states. There is, apparently, a general agreement that the transition phenomena are primarily lattice dominated, but a band structure which will satisfy both electrical and optical considerations has not yet been formulated.

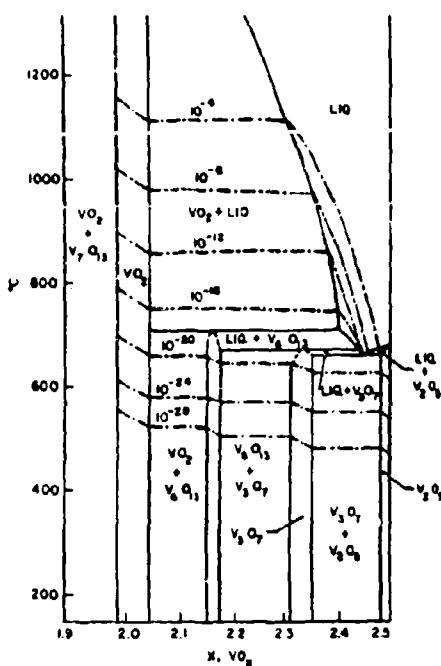
In general, electrical and magnetic data yield a one-electron band model with relatively large electron-phonon interactions. In a band structure derived from optical data, Verleur et al. propose a model for  $\text{VO}_2$  above the transition temperature, in which filled valence bands (associated with the oxygen) are separated from partially filled conduction bands (arising from the vanadium), with the lowest vanadium bands slightly overlapping one or more of the partially filled bands. On this basis, the  $\text{VO}_2$  at temperatures above the transition, would be a semi-metal, rather than a metal. In the model derived from optical data,  $\text{VO}_2$  at temperatures below the transition would have electrons trapped in localized levels or occupying two completely filled bands. In any event, much more experimental data on crystals of high purity and stoichiometric quality are needed to choose a realistic band structure model.

Repeated cycling of crystals of  $\text{VO}_2$  causes cracking and to obviate this difficulty, Hensler, Fuls, Rozgony and their associates have prepared sputtered, polycrystalline films, 500 to 4000 Å thick, annealed at 400°C. These randomly oriented thin films, when carried through the heating and cooling cycle, show new random configurations with the same properties as previously and may, therefore be considered stable.

Vanadium monoxide is stable over a composition range of  $\text{VO}_{0.8}$  to  $\text{VO}_{1.3}$ . Density measurements indicate that stoichiometric samples are highly defective and analysis of Infrared spectra by Ariya & Golomolzina led them to the conclusion that the monoxide comprises regions of vanadium alternating with regions of  $\text{V}_2\text{O}_3$ .

The data tables which follow, cover all vanadium oxides known to date, including those which do not show any phase transition. Pertinent curves for the several properties covered in the tables are inserted, following each stoichiometric compound. A few graphs have been included for chromium, aluminum or titanium doped vanadium oxides for their value in device applications, but these materials will be more fully covered in a later report.

PHASE DIAGRAM

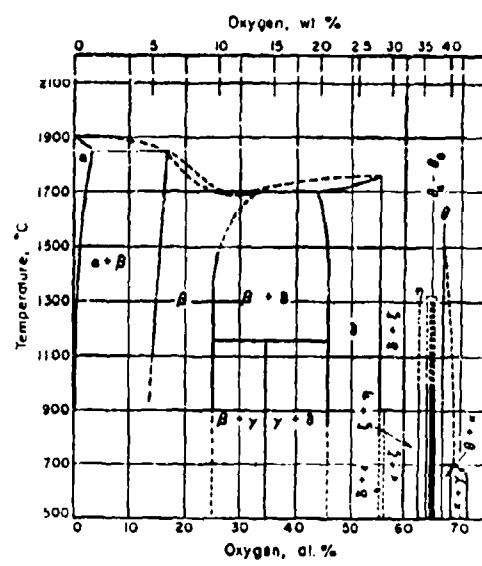


Vanadium-Oxygen phase diagram, on the basis of recent data.

— · — · · · oxygen partial pressure (atm)  
— · — · estimated oxygen pressure

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MacChesney & Guggenheim,  
Kosuge, B  
MacChesney et al.



Vanadium-Oxygen System

Stringer

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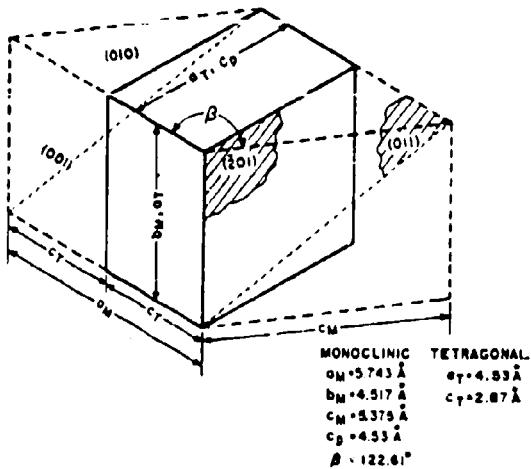
Phase Analyses of vanadium oxides by magnetic susceptibility measurements and x-ray diffraction measurements.

Kosuge, B

$\text{VO}_2$	Phase	$\text{VO}_2$	Phase	$\text{VO}_2$	Phase
1.50	$\text{V}_2\text{O}_3$	1.84	$\text{V}_6\text{O}_{11} + \text{V}_2\text{O}_3$	2.30	$\text{V}_6\text{O}_{13} + \text{V}_2\text{O}_7$
1.51	$\text{V}_2\text{O}_3$	1.85	$\text{V}_6\text{O}_{11} + \text{V}_2\text{O}_3$	2.32	$\text{V}_2\text{O}_7$
1.52	$\text{V}_2\text{O}_3 + \text{V}_3\text{O}_5$	1.86	$\text{V}_2\text{O}_3$	2.34	$\text{V}_3\text{O}_7$
1.64	$\text{V}_3\text{O}_5 + \text{V}_2\text{O}_3$	1.87	$\text{V}_2\text{O}_3 + \text{VO}_2$	2.36	$\text{V}_3\text{O}_5 + \text{V}_2\text{O}_5$
1.65	$\text{V}_3\text{O}_5$	1.97	$\text{VO}_2 + \text{V}_2\text{O}_3$	2.38	$\text{V}_3\text{O}_5 + \text{V}_2\text{O}_5$
1.66	$\text{V}_3\text{O}_5$	1.98	$\text{VO}_2 + \text{V}_2\text{O}_3$	2.40	$\text{V}_3\text{O}_5 + \text{V}_2\text{O}_5$
1.67	$\text{V}_3\text{O}_5$	1.99	$\text{VO}_2$	2.42	$\text{V}_3\text{O}_5 + \text{V}_2\text{O}_5$
1.68	$\text{V}_3\text{O}_5 + \text{V}_4\text{O}_7$	2.00	$\text{VO}_2$	2.45	$\text{V}_3\text{O}_5 + \text{V}_2\text{O}_7$
1.73	$\text{V}_3\text{O}_5 + \text{V}_3\text{O}_5$	2.01	$\text{VO}_2$	2.47	$\text{V}_2\text{O}_3 + \text{V}_3\text{O}_7$
1.74	$\text{V}_4\text{O}_7$	2.02	$\text{VO}_2$	2.48	$\text{V}_2\text{O}_3$
1.75	$\text{V}_4\text{O}_7$	2.03	$\text{VO}_2 + \text{V}_2\text{O}_3$	2.50	$\text{V}_2\text{O}_3$
1.76	$\text{V}_4\text{O}_7 + \text{V}_3\text{O}_5$	2.10	$\text{VO}_2 + \text{V}_2\text{O}_3$		
1.77	$\text{V}_3\text{O}_5 + \text{V}_4\text{O}_7$	2.15	$\text{V}_6\text{O}_{11} + \text{VO}_2$		
1.78	$\text{V}_6\text{O}_{11} + \text{V}_4\text{O}_7$	2.16	$\text{V}_6\text{O}_{11}$		
1.79	$\text{V}_6\text{O}_{11} + \text{V}_4\text{O}_7$	2.166	$\text{V}_6\text{O}_{11}$		
1.80	$\text{V}_6\text{O}_{11}$	2.17	$\text{V}_6\text{O}_{11}$		
1.81	$\text{V}_6\text{O}_{11} + \text{V}_6\text{O}_{11}$	2.18	$\text{V}_6\text{O}_{13} + \text{V}_3\text{O}_7$		
1.82	$\text{V}_6\text{O}_{11} + \text{V}_6\text{O}_{11}$	2.20	$\text{V}_6\text{O}_{13} + \text{V}_3\text{O}_7$		
1.83	$\text{V}_6\text{O}_{11}$	2.25	$\text{V}_6\text{O}_{13} + \text{V}_3\text{O}_7$		

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## CRYSTAL STRUCTURE



$\text{VO}_2$

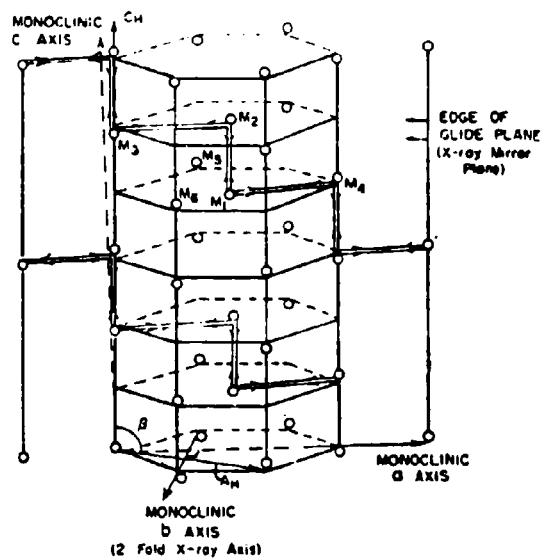
Relation between tetragonal unit  
(high temperature, solid lines)  
and monoclinic unit (low temperature,  
dashed lines).

Major monoclinic planes are shown.

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Simplified structure of  $\text{V}_{23}$   
showing only the vanadium ion  
position.

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THE VANADIUM-OXYGEN SYSTEM

PHYSICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula	V0					
Stability range	VO <sub>0.8</sub> -VO <sub>1.3</sub>			(Possible: V0= V+V <sub>2</sub> O <sub>3</sub> )		Stringer, Adler
Molecular Wgt.		66.95				
Density		5.92	g/cm <sup>3</sup>	6.49 (calc.)		Donnay
Color		light grey				Handbook
Symmetry		cubic				Donnay
Space Group		Fm3m Z-4				Donnay
Lattice Parameters	a <sub>0</sub>	4.099	Å			Massard et al.
		4.093				Donnay
	V-V	2.93				Bongers
VO <sub>x</sub>	a <sub>0</sub> (Å)	Density (g/cc)	Vacancies (%)			
0.86	4.034	5.736	37.0	sintered at 1300°C		Banus et al.
0.96	4.058	5.674	31.7			
0.99	4.068	5.602	30.8			
1.02	4.077	5.583	28.9			
1.23	4.133	5.329	21.2			
1.30	4.14	5.85	22	single crystal, zero oxygen vacancies		
Melting Point		1720	°C	in vacuo		Stringer
Specific Heat		0.014 0.158 0.225	cal/g °K		50 300 1700	TPRC, p. 528

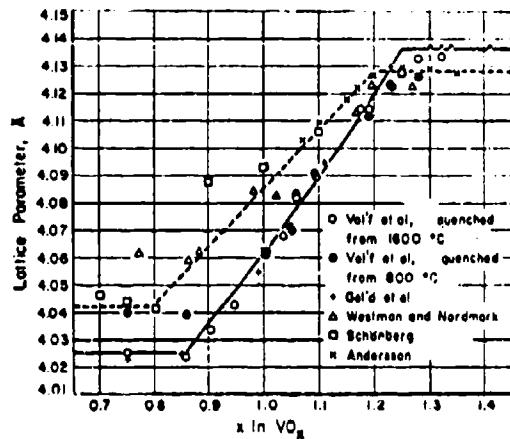
THE VANADIUM-OXYGEN SYSTEM

ELECTRICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Resistivity	$VO_{0.83-0.86}$	$VO_{1.02}$	$VO_{1.2}$			
	$8 \times 10^{-4}$	$6 \times 10^{-3}$	Ω-cm	sintered	4	Honig et al.
	$8 \times 10^{-4}$	$5 \times 10^{-3}$	$9 \times 10^{-1}$	sintered, shows no $T_c$	77	Banus et al.
	$8 \times 10^{-4}$	$2 \times 10^{-3}$	$10^{-2}$		300	
	$VO_{0.919}$	$VO_{1.147}$	$VO_{1.25}$			
	$2 \times 10^{-3}$	$3 \times 10^{-2}$	— Ω-cm	sintered to 90% density, shows no $T_c$	100	Kawano et al. [A]
	$10^{-3}$	$2 \times 10^{-2}$	$2 \times 10^{-1}$		115	
	$8 \times 10^{-4}$	$5 \times 10^{-3}$	$6 \times 10^{-3}$		300	
		$2 \times 10^{-3}$	Ω-cm	1-5μ, epitaxial film on MgO, no $T_c$	77-300	Takei & Koide [A]
		$0.4 \times 10^{-3}$		0.3μ film, $VO_{0.2}$	300	Hensler et al.
		$0.8 \times 10^{-3}$		0.1μ film, $VO_{1.2}$		
Temp. Coeff.		$-3 \times 10^{-5}$	°C <sup>-1</sup>	0.3μ film, $VO_{0.2}$		Hensler et al.
		$-10^{-3}$		0.1μ film, $VO_{1.2}$		
Resistivity		$10^7$	Ω-cm	$VO_{0.9}$	94	Austin
		$10^6$		$VO$ , single crystal	83	Morin
		$10^{-2}$			300	
Transition Temp. $T_c$		114 126	°K	cooling heating		Morin
Pressure Coeff.	$dT_c/dP$	-3	$10^3$ °K/bar	$P = 25$ kbars	94, 113	Austin
Transition Temp.		88-125	°K	NMR meas., range due to variations in stoichiometry		Warren et al.

THE VANADIUM-OXYGEN SYSTEM

ELECTRICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Energy Gap		6	meV	high V content		Banus et al., Kawano et al. [A]
		0.157	eV	low V content		
Seebeck Coeff.	V <sub>O</sub> .88	V <sub>O</sub> .99	V <sub>O</sub> 1.05	V <sub>O</sub> 1.23		Banus et al.
	-12	-4	+5	+22 $\mu$ V/°K	sintered	
Magnetic Susceptibility $\chi_q$	V <sub>O</sub> .85	V <sub>O</sub>	V <sub>O</sub> 1.05	V <sub>O</sub> 1.26		Kawano et al. [B]
	-5	+3	+8	+26	sintered to 90% density	
	0	+3	+17			
Magnetic Susceptibility $\chi_q$	6		$10^{-6}$ cgs	sintered, V <sub>O</sub>	300	Massard et al.
	8			sintered	90	Bogdanova & Loginov
	5				300	
	V <sub>O</sub> .92	V <sub>O</sub> 1.07	V <sub>O</sub> 1.26			Kawano et al. [A]
	25	80	115	$10^{-6}$ cgs	sintered	

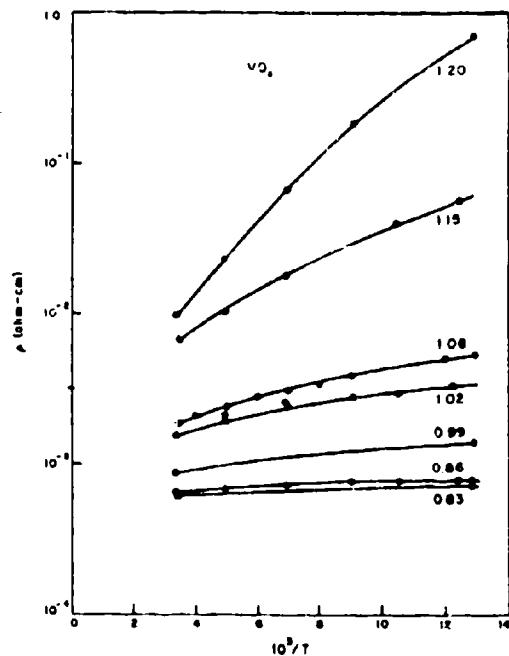
$V_0$  0.7-1.4



Lattice Parameters as a function of composition.

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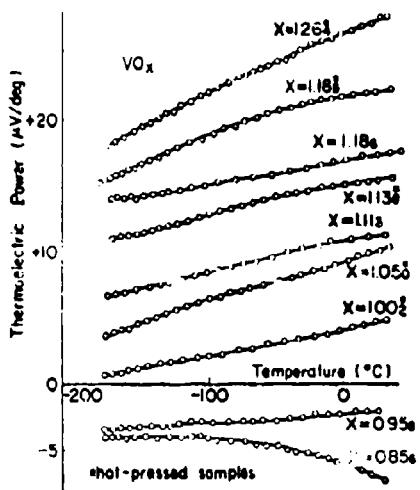
Stringer



Electrical resistivity as a function of temperature and composition for sintered samples.

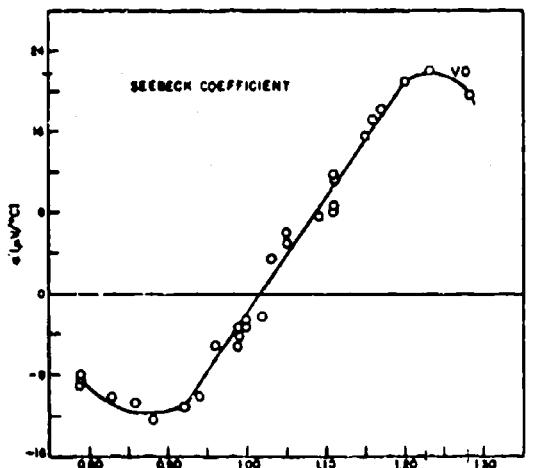
Banus et al.

$\text{VO}_{0.7-1.4}$



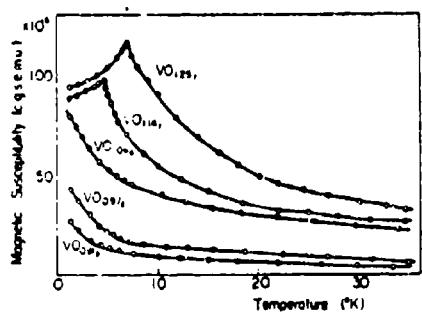
Thermoelectric power as a function  
of temperature for sintered  $\text{VO}_x$

Kawano et al., B



Thermoelectric power as a function  
of composition in sintered  $\text{VO}_x$

Banus et al.



Magnetic susceptibility as a function  
of temperature for sintered  $\text{VO}_x$

Kawano et al., B

THE VANADIUM-OXYGEN SYSTEM

PHYSICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		VO <sub>2</sub>				
Molecular Wgt.		82.94				
Density		4.69	g/cm <sup>3</sup>			Donnay
Color		blue				Handbook
Symmetry		monoclinic				Donnay
Space Group		P2 <sub>1</sub> /a Z-4				Donnay
Lattice Parameters	a <sub>0</sub> b <sub>0</sub> c <sub>0</sub> β	5.744 4.520 5.376 122.6	Å			Rao et al.
	V-V	2.65, 3.12	Å			Everhart & McChesney
Transition Temperature		68	°C	to rutile structure		Chamberland
Symmetry		tetragonal		(rutile)		Donnay
Lattice Parameters	a <sub>0</sub> c <sub>0</sub>	4.559 2.801	Å		357	Rao et al.
	V-O O-O	1.95 2.50, 2.87				Bongers, Westman
Temperature (1/a)(da/dT) Coeff. (1/c)(dc/dT)	0.5 3.6	10 <sup>-5</sup>	/°K		340-550	Bongers
Melting Point		1818	°K			Cook, TPRC, p. 532
Specific Heat		0.157	cal/g °K		300	TPRC, Berglund & Guggenheim
		0.25			1700-1900	TPRC

### THE VANADIUM-OXYGEN SYSTEM

PHYSICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Debye Temperature		750	°K		300	Berglund & Guggenheim, Derbenwick
Thermal Conductivity		65	mW/cm °K		300-360	Berglund & Guggenheim
Thermal Expansion Coefficient		24	$10^{-6}/^{\circ}\text{K}$	monoclinic, single crystal,    c-axis	68°C	Guntersdorfer
	-a	26	$10^{-6}/^{\circ}\text{K}$	tetragonal, single crystal	137°C	Hazony & Perkins, Bongers
Young's Modulus		2	$10^{12}$ dynes/cm <sup>2</sup>	monoclinic	300	Guntersdorfer
<b>ELECTRICAL PROPERTIES</b>						
Dielectric Constant		$\epsilon \perp a$	$\epsilon \parallel a$			
Optic	$\epsilon_{\omega}$	10.0	9.7			
Static	$\epsilon_0$	40.6	25.9	reflectivity meas. at 1-90μ on single monoclinic crystal	300	Barker et al.
Optic						
Monoclinic		5.6	5.54	at 0.3-6μ	300	Verleur et al.
Monoclinic			4.26	1000 Å film at 0.25 to 4μ	300	
Tetragonal			3.95	1000 Å film at 0.25 to 6μ	355	
Optic		0.6	1.2μ			
Monoclinic		8.5	9.5	single crystals & sputtered films	300	Derbenwick
Tetragonal		6	-1		350	
Optic		$\epsilon \perp a$	$\epsilon \parallel a$			
Tetragonal		3.77	4.17	single crystal at 0.25 to 3μ	355	Verleur et al.

THE VANADIUM-OXYGEN SYSTEM

ELECTRICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
<b>Dielectric Constant</b>						
Pressure Coeff.						
	$(1/\epsilon)(d\epsilon/dP)$	-2	$10^{-6}$ /bar			Neuman et al.
Resistivity		$5 \times 10^{-4}$	Ω-cm	high purity, single crystal	293 341	Bongers, McChesney & Guggenheim, Bando et al., Ladd & Paul
		$5 \times 10^3$		single crystal	4	Austin & Turner
		$10^{-5}$	f (Hz)	single crystal, $\parallel$ -[100]	300	Kabashima et al.
		100	$10^3-10^8$			
		25	$10^{10}$			
<u><math>\parallel</math>c-axis    <math>\parallel</math>a-axis</u>						
		$4 \times 10^{-2}$	$10^{-2}$ Ω-cm	epitaxial films on rutile	300	Koide & Takai
		$2 \times 10^{-3}$	$4 \times 10^{-4}$	monoclinic crystals	300	Everhart & McChesney
Temperature Coeff.	$\Omega\text{-cm}$	TCR	Thickness			
	4.2	$-0.036/^\circ\text{C}$	700 Å	sputtered films	300	Hensler et al.
	2.3	$-0.106/^\circ\text{C}$	1000			
Pressure Coeff.						
	$d\rho/d\rho P$	-2 -3.5	$10^{-5} \text{ cm}^2/\text{kg}$	single crystal, $P = 5 \times 10^3 \text{ kg/cm}^2$	293	Ladd & Paul, Guntersdorfer, Neumann et al.

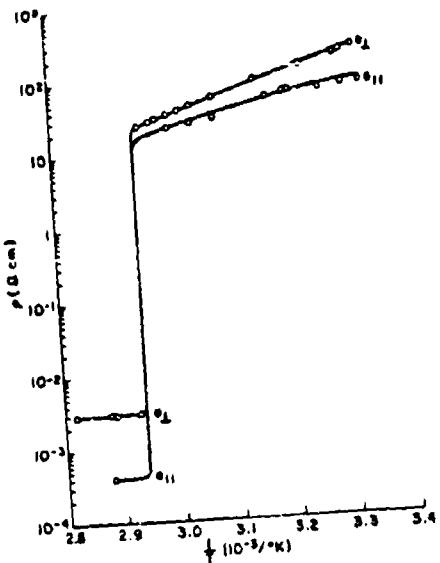
THE VANADIUM-OXYGEN SYSTEM

ELECTRICAL PROPERTIES	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Transition Temperature	T <sub>c</sub>	68°C				Chamberland
Pressure Coeff.	dT <sub>c</sub> /dP	+8.02	10 <sup>-5</sup> °K/kg cm <sup>-2</sup>	single crystal, P= 4x10 <sup>4</sup> kg/cm <sup>2</sup> dp= 10 <sup>4</sup> Ω-cm		Berglund & Jayaraman
		+5.90		high purity, single crystal, P= 8x10 <sup>3</sup> kg/cm <sup>2</sup>		Ladd & Paul, Neumann et. al.
Transition Time		20	nsec.	1600 Å thick film, sputtered on glass		Roach & Balberg, Cope & Penr.
Mobility		0.05 0.01	cm <sup>2</sup> /V sec	sputtered film, powder	273 370	Hensler, Kitahiro et al.
		0.6 15-20		single crystal, 1 Ω-cm	300 353	Barker et al.
Effective Mass						
Electron	m <sub>n</sub>	0.5-4	m <sub>o</sub>	metallic state, calc. from optical and electric meas.	>68°C	Barker et al., Berglund & Guggenheim
	m <sub>dn</sub>	1.6-7		semiconducting state	<68°C	
	m <sub>n</sub>	1-4				
	m <sub>n</sub>	7.1		single crystal, sputtered films	>68°C	Hensler
		1			<68°C	
Energy Gap		0.6-0.7	eV	optical meas. at 0.3-6μ on a film, electrical meas. on a single crystal, photoemission meas. on a film	<68°C	Verleur et al., Heywang & Gunthersdorfer, Powell et al.

## THE VANADIUM-OXYGEN SYSTEM

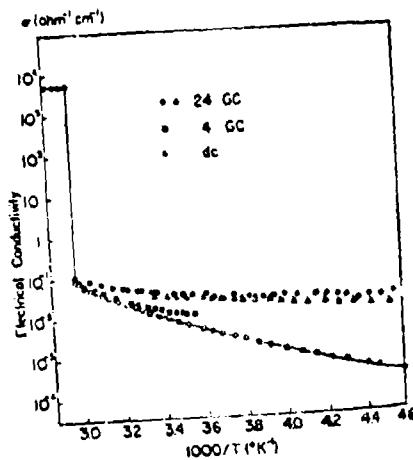
ELECTRICAL PROPERTIES	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Energy Gap						
Pressure Coeff.	$dE_g/dP$	$\sim 10^{-6}$	eV/kg cm <sup>-2</sup>	semiconducting state		Berglund & Jayaraman
Deformation Potential		8	eV	piezoresistance meas. on single crystal	300	Guntersdorfer
Photoemission Threshold		5.4 4.8	eV	5μ film	298 373	Powell et al.
Quantum Yield		$7 \times 10^{-3}$ $2 \times 10^{-2}$	electrons/proton		298 373	Powell et al.
Seebeck Coeff.		-21.1 -23.1 -30 to -400	μV/°C	c-axis ⊥ c-axis	75°C 300	Berglund & Guggenheim, Hensler
		-900 -750		single crystal	293 333	Kitahiro & Watanabe, Bongers
		-130		700-1300 Å, single crystal, sputtered films	300	Hensler
Magnetic Susceptibility	$\chi_g$	0.88	$10^{-6}$ cgs	single crystals	100-300	Barker et al., Hill & Martin
		1.0 7.9	$10^{-6}$ cgs	⊥-c     -c	293-340 340-373	Berglund & Guggenheim
Reflectivity		metallic		$\lambda = 0.7-0.8\mu$	70°C	Mokerov & Rakov, Barker et al.
Emissivity		2.5 4.4 2.0	$10^{-2}$ W/cm <sup>2</sup>	single crystal	300 340 341	Boyle & Verleur

$\text{VO}_2$  - ELECTRICAL RESISTIVITY



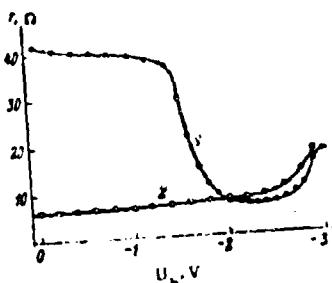
Resistivity of single crystal  $\text{VO}_2$  as a function of temperature, measured parallel and normal to the monoclinic  $a$ -axis.

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The dc and microwave conductivities of single crystals, as a function of temperature.

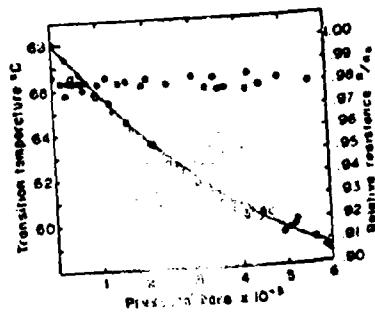
Kabashima et al.



Resistance as a function of bias voltage at 296 K.

1. Increasing voltage
2. Decreasing voltage

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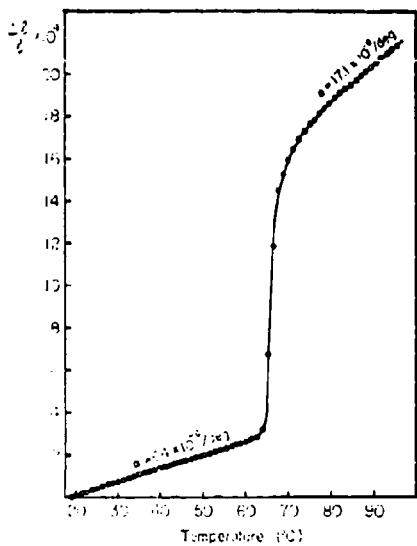


Pressure dependence of the transition temperature in single crystal  $\text{VO}_2$  at  $24.5^\circ\text{C}$

- increasing pressure
- △ decreasing pressure
- resistance normalized to atmospheric pressure

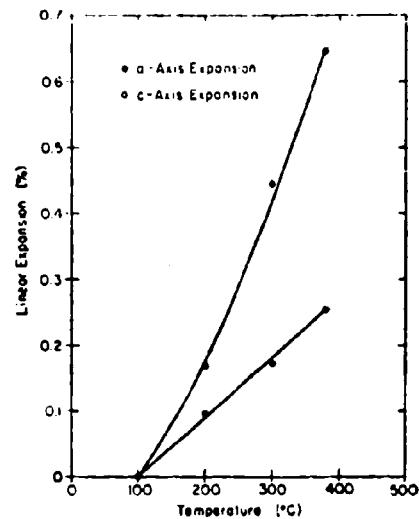
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## $\text{VO}_2$ - PHASE TRANSITION



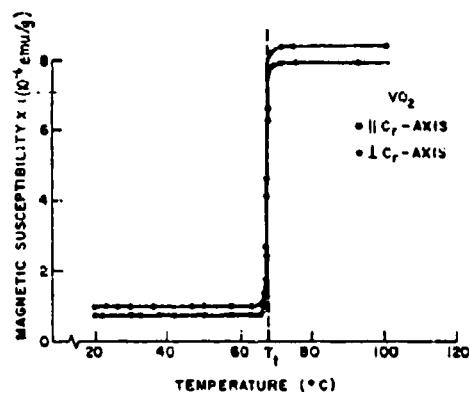
Thermal expansion as a function of temperature for sintered  $\text{VO}_2$

Kawakubo & Nakagawa



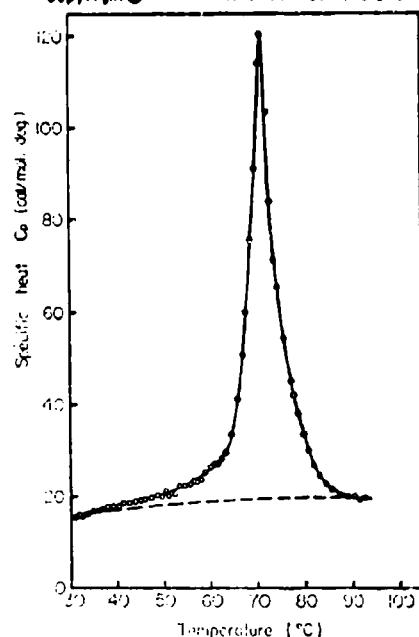
Thermal expansion of tetragonal  $\text{VO}_2$  along two axes.

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Magnetic susceptibility as a function of temperature in single crystal  $\text{VO}_2$  near the transition temperature.  
Measurements are parallel and normal to the rutile  $c$ -axis.

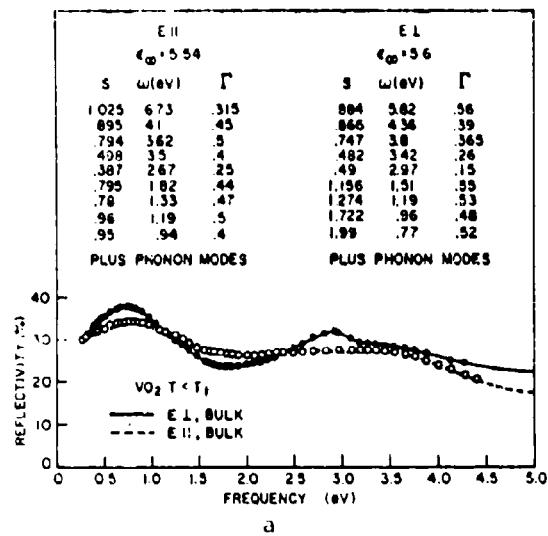
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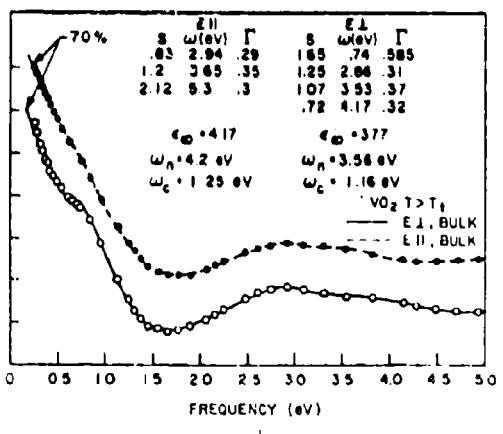
Specific heat as a function of temperature for sintered  $\text{VO}_2$

Kawakubo & Nakagawa

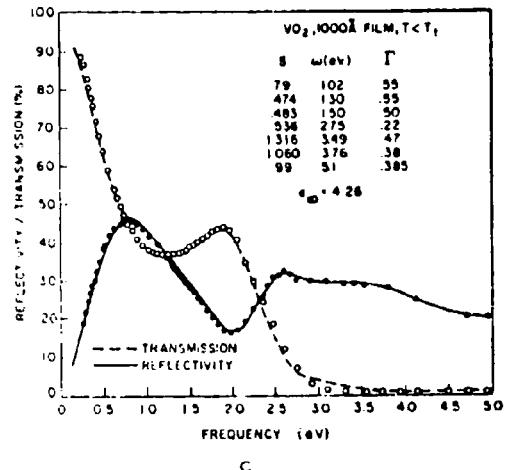
## $\text{VO}_2$ - OPTICAL PROPERTIES



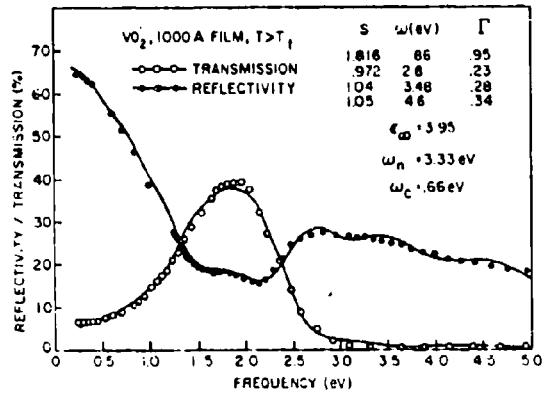
a



b



c



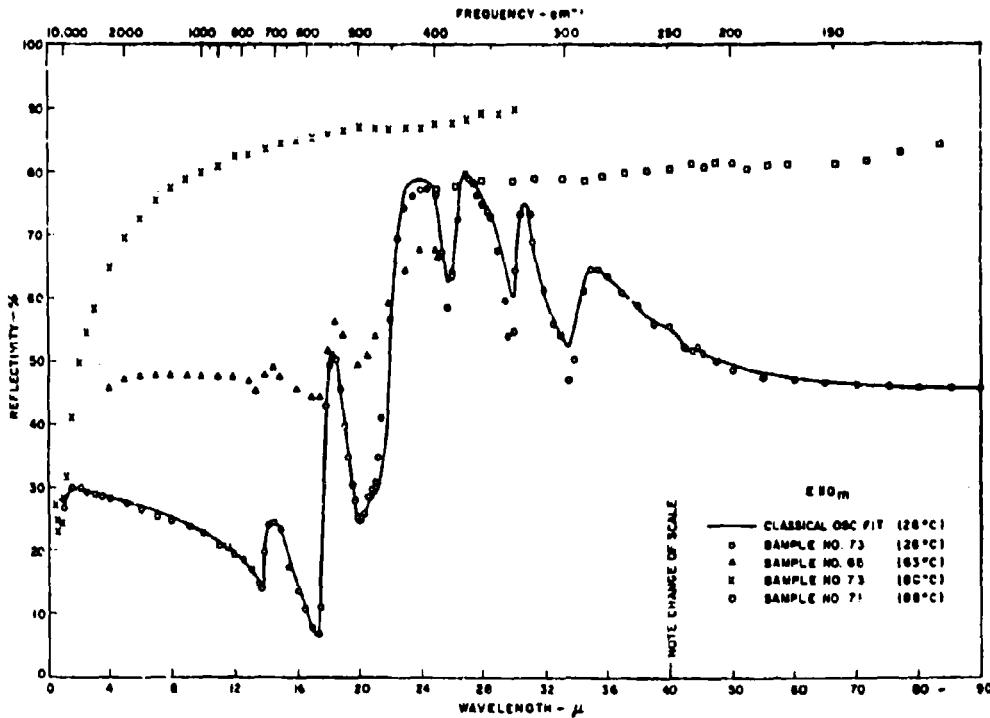
d

Reflectivity/Transmission data as a function of photon energy for single crystals and films of vanadium dioxide. The classical oscillator fit is shown at 300°K as well as slightly above the transition temperature, 355°K

- a. bulk single crystals at 300°K
- b. bulk single crystals at 355°K
- c. 1000 Å film on sapphire substrate at 300°K
- d. 1000 Å film on sapphire substrat. at 355°K

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Verleur et al.

## VO<sub>2</sub> - REFLECTIVITY



Reflectivity as a function of wavelength at three temperatures.  
The solid curve is a fit for data below the transition temperature,  
at 63°C. Data points marked by a triangle were taken on cooling.

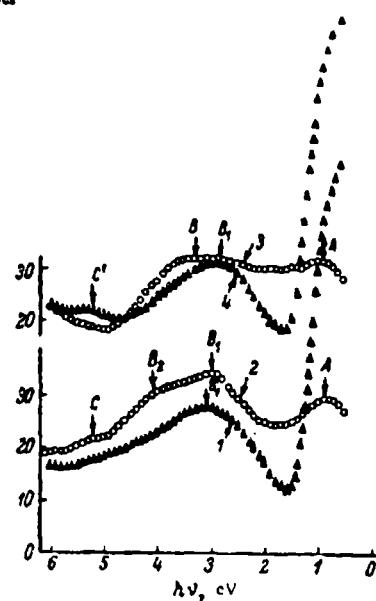
Published with permission Barker et al.  
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Reflectivity as a function of wavelength  
for single crystals, measured above and  
below the transition temperature.

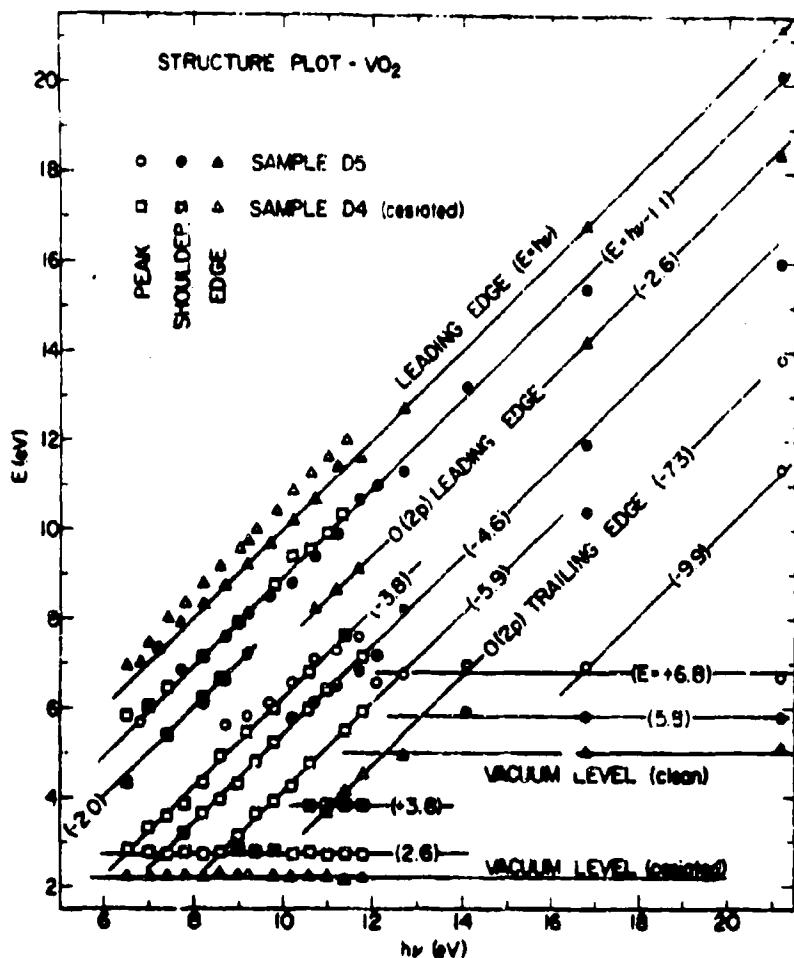
1.  $E \perp c_r$  above 70°C
2.  $E \perp a_m$  at 20°C
3.  $E \parallel a_m$  at 20°C
4.  $E \parallel c_r$  above 70°C

Structure above 2 eV is associated with  
electron transitions; below 2 eV the  
reflectivity is metallic.

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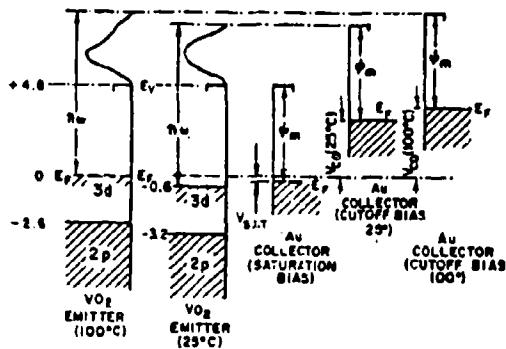


VO<sub>2</sub> - BAND STRUCTURE



Electron energy,  $E$ , is measured relative to the uppermost occupied level. The location of the structure relative to the uppermost occupied level is the same for V<sub>2</sub>O<sub>4</sub> and V<sub>4</sub>O<sub>8</sub> within the resolution of the photoemission.

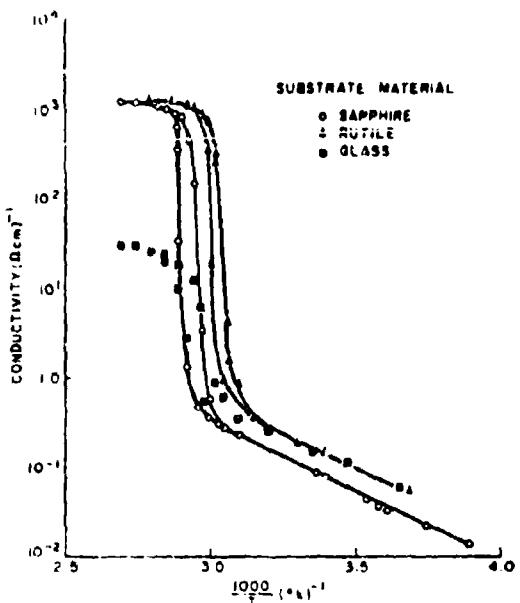
Derbenwick



Energy level and bias relationships for VO<sub>2</sub> above and below the transition temperature.  $E_F$  is the Fermi level and  $E_V$  marks the vacuum level. The energy zero point is placed at the Fermi level.

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## $\text{VO}_2$ - FILMS



Electrical Conductivity as a function of temperature for  $\text{VO}_2$  films.

Curves show the effects of various substrates on the transition temperature.

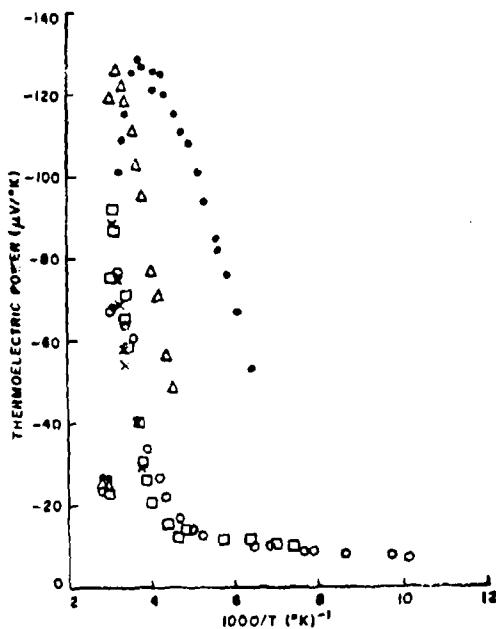
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Rozgonyi & Hensler

Thermoelectric power as a function of temperature for  $\text{VO}_2$  films of varied thickness, deposited on various substrates.

- |   |                         |             |
|---|-------------------------|-------------|
| X | $\text{Al}_2\text{O}_3$ | 670 Å thick |
| ◻ | "                       | 1500 Å      |
| ○ | $\text{TiO}_2$          | 1500 Å      |
| △ | $\text{Al}_2\text{O}_3$ | 1300 Å      |
| ● | "                       | 1300 Å      |

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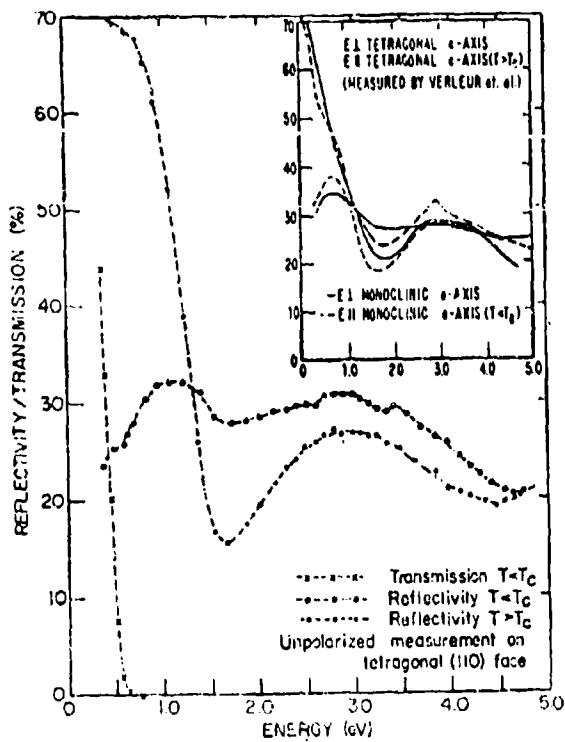
THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		V <sub>2</sub> O <sub>4</sub>				
Molecular Wt.		165.884				
Density		4.4	g/cm <sup>3</sup>			Cook
Symmetry		monoclinic			<70°C	Chamberland, Minomura & Nagasaki
Lattice Parameters	a <sub>0</sub>	5.753	°A		335	Chamberland, Minomura & Nagasaki
	b <sub>0</sub>	4.524				
	c <sub>0</sub>	5.382				
	β	122.62°				
Symmetry		tetragonal		(rutile)	>/0°C	Minomura & Nagasaki, King & Suber
Lattice Parameters	a <sub>0</sub>	4.54	°A		344	Minomura & Nagasaki
	c <sub>0</sub>	2.85				
Coefficient of Expansion		5.4	10 <sup>-6</sup> /°K	(tetragonal)		King & Suber
Shift in Coefficient		-1	10 <sup>-4</sup> /°K		67°C	Minomura & Nagasaki
Melting Point		1547	°C			TPRC, p. 532, Cook
Specific Heat		0.18 0.25 0.25	cal/g°K		300 1700 1800	TPRC, p. 532

THE VANTZIUM-OXYGEN SYSTEM

ELECTRICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Dielectric Constant						
Optical	$\epsilon_{\infty}$	9		tetragonal, E  c-axis	353	Barker et al.
Resistivity		$10^{-4}$	$\Omega\text{-cm}$	single crystal, high quality, oriented   c-axis	>339 <339	Ladd & Paul
Transition Temperature		66	°C			Ladd & Paul
Pressure Coeff.	$dT_c/dP$	6	$10^{-5} \text{ }^{\circ}\text{K/bar}$	P= 8 kbars		Ladd & Paul
Resistivity		$10^{-2}$	$\Omega\text{-cm}$	amorphous film, rf-sputtered on substrate at 135°C	300	MacKenzie
Energy Gap	$E_g$	0.65	eV	transmission meas. on single crystal	300	Ladd & Paul

### $V_2O_4$ - REFLECTIVITY

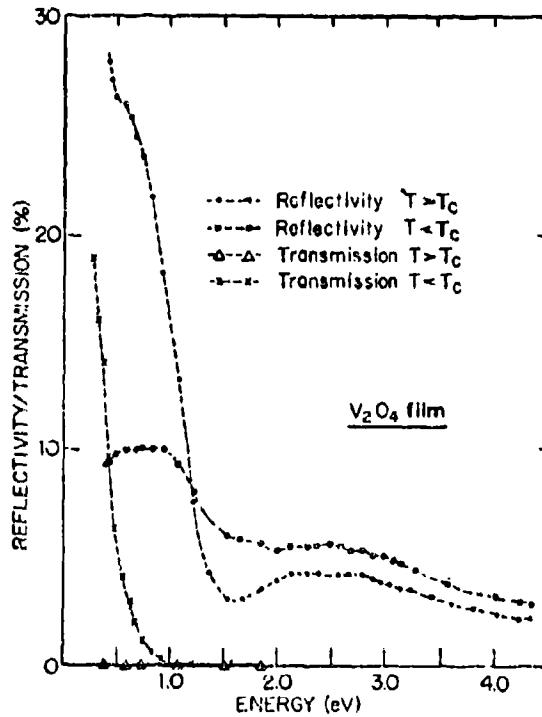


Reflectivity/Transmission as a function of wavelength in a single crystal, above and below the transition temperature, (300 and 360°K). Transmission is also shown for a thin sample at 300°K

Fan & Paul

Reflectivity/Transmission of a single crystal, epitaxial film, grown by vapour transport. Data are taken above (350°K) and below (300°K) the transition temperature.

Fan & Paul



## THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		V <sub>5</sub> O <sub>9</sub>		VO <sub>1.8</sub>		Kosuge [B]
Molecular Wgt.		398.71				
Symmetry		triclinic				Donnay
Lattice Parameters	a <sub>0</sub>	7.004	Å			Donnay
	b <sub>0</sub>	7.825				
	c <sub>0</sub>	5.465				
	α	97°39'				
	β	109° 2'				
	γ	94° 6'				
Density		4.72	g/cm <sup>3</sup>			Donnay
Electrical Resistivity		10 <sup>-3</sup> 10 <sup>3</sup> -10 <sup>4</sup>	Ω-cm	single crystal	130-300 125	Okinaka et al. [D]
Transition Temperature		130	°K	single crystal		Okinaka et al. [D]
Seebeck Coeff.		-10 to -20	µV/°K	single crystal	130-300	Okinaka et al. [D]
		-200			125	
		-800			110	
Magnetic Susceptibility	X <sub>g</sub>	10	10 <sup>-6</sup> cgs	single crystal	77-140	Nagasawa et al. [A]
		45			140	Kosuge [B]
		28			265	
Néel Temperature		162	°K	sintered		Kosuge et al. [A]

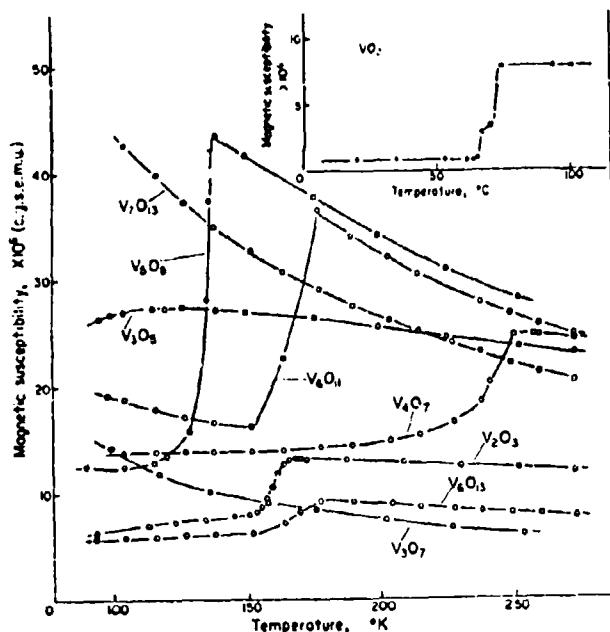
THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		V <sub>6</sub> O <sub>13</sub>		V <sub>2</sub> O <sub>3</sub> .16-2.17		Kosuge [B]
Molecular Wgt.		513.652				
Melting Point		708	°C			Kosuge [B]
Symmetry		monoclinic		V <sub>12</sub> O <sub>26</sub>		Donnay
Lattice Parameters	a <sub>0</sub>	11.90				Donnay
	b <sub>0</sub>	3.671				
	c <sub>0</sub>	10.122				
	β	100°52'				
Expansion Coeff.		-1.62 +1.14	10 <sup>-4</sup> /°K 10 <sup>-5</sup> /°K	sintered	80-173 173-300	Kosuge et al. [B]
Electrical Resistivity		10 <sup>3</sup> 3x10 <sup>5</sup> 2x10 <sup>4</sup> 2.5x10 <sup>6</sup>	Ω-cm	sintered	300 156 157 100	Kachi et al.
Transition Temperature		156 154	°K	electrical meas. magnetic meas.		
Pressure Coeff.	dT <sub>C</sub> /dP	-1.06	10 <sup>-4</sup> °K/bar	single crystal		Kosuge et al. [B]
Magnetic Susceptibility	X <sub>g</sub>	6 9 8	10 <sup>-6</sup> cgs	sintered	77-150 175 280	Kosuge et al. [A,B]
Néel Temperature		155	°K			Kosuge et al. [A]

THE VANADIUM-OXYGEN SYSTEM

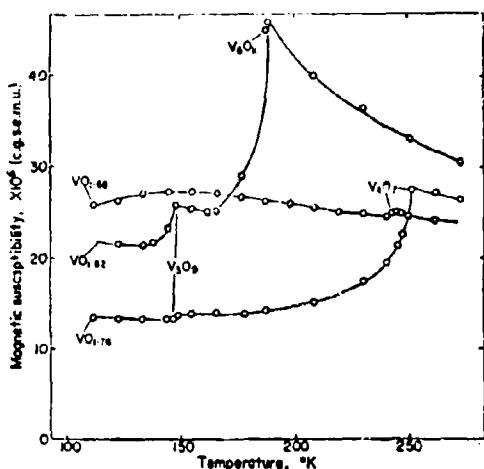
PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		V <sub>6</sub> O <sub>11</sub>		V01.83		Kosuge[B]
Molecular Wgt.		481.652				
Electrical Resistivity		10 <sup>-1</sup> 10 <sup>2</sup>	Ω-cm	single crystal 177	177-300 177	Okinaka et al.[C]
Transition Temperature		177	°K			Okinaka et al.[C]
Seebeck Coeff.		-10 -900	μV/°K	single crystal	177-300	Okinaka et al.[C]
Magnetic Susceptibility	X <sub>g</sub>	20 36 31	10 <sup>-6</sup> cgs	single crystal, T <sub>c</sub> = 170°K	77 170 250	Nagasawa et al.[B], Kosuge[B]
Formula		V <sub>7</sub> O <sub>13</sub>		single crystal		Okinaka et al.[C]
Electrical Resistivity		10 <sup>-3</sup>	Ω-cm		120-300	
Seebeck Coeff.		-1	μV/°K		120-300	
Magnetic Susceptibility	X <sub>g</sub>	44 22	10 <sup>-6</sup> cgs		100 250	Kosuge[B]
Formula		V <sub>4</sub> O <sub>7</sub>		single crystal		Okinaka et al.[E]
Electrical Resistivity		10 <sup>-2</sup> 2x10 <sup>-3</sup> 10 <sup>2</sup>	Ω-cm		300 250 200	
Seebeck Coeff.		-10 -230	μV/°K		250-300 200	
Transition Temperature		250	°K			
Magnetic Susceptibility	X <sub>g</sub>	14 24	10 <sup>-6</sup> cgs		100-175 250-260	Kosuge[B]

VANADIUM DIOXIDES



Magnetic susceptibility as a function of temperature for a series of vanadium dioxides.

Kosuge, B

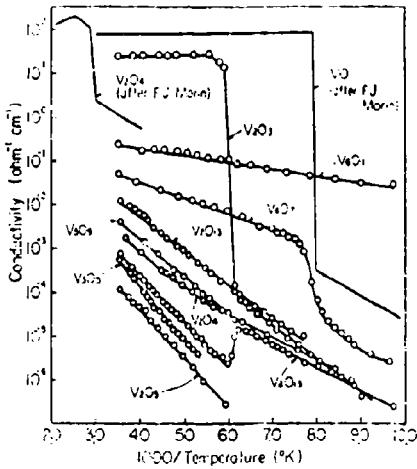


Magnetic susceptibility as a function of temperature, employed for the phase identification of a series of non-stoichiometric  $\text{V}_2\text{O}_4$  compounds.

Kosuge, B

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## VANADIUM DIOXIDES



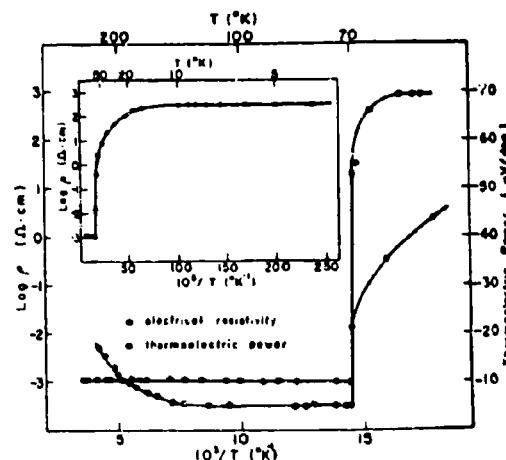
Electrical conductivity as a function of temperature for a series of vanadium oxides.

Kachi et al.

Electrical resistivity and thermoelectric power for  $V_8O_{15}$  as a function of temperature. The insert shows the electrical resistivity-temperature curve down to 4°K

Okinaka et al., B

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THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		V <sub>2</sub> O <sub>5</sub>				
Molecular Weight		181.88				
Density		3.357 2.42-2.69	g/cm <sup>3</sup>	single crystal amorphous	298	Kennedy et al.
Color		pale yellow		transparent		Kenny et al.
Cleavage		(100)		acicular habit		Donnay
Symmetry		orthorhombic				Donnay
Space Group		Pnm2 Z-2				Donnay
Lattice Parameters	a <sub>0</sub> b <sub>0</sub> c <sub>0</sub>	11.510 4.369 3.563	Å			Bachmann et al.
Melting Point		668 676	°C	single crystal, loses oxygen on heating in vacuo at 600°C		Kennedy et al.
Specific Heat		0.167 0.227	cal/g°K		300 950	TPRC, p. 534
Thermal Expansion Coefficient		2 55.4 8	10 <sup>-6</sup> /°K	a-axis    b-axis    c-axis	25-600°C	Kennedy et al.
ELECTRICAL PROPERTIES						
Dielectric Constant						
Optical	ε <sub>∞</sub>	~ 4				Kenny et al.

THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
<b>Dielectric Constant</b>						
Static	$\epsilon_0$	6.89		pressed powder at 6 GHz	300	Kiriashkina et al.
<b>Resistivity</b>						
	a	b	c (axes)			
	170	4700	670 ohm-cm	single crystal	298	Kennedy et al.
	$5 \times 10^8$	$10^{10}$	$2 \times 10^8$	single crystal platelets grown at 700°C, laminar	100	McCulloch
	$10^3$	$2 \times 10^3$	$5 \times 10^2$	with mirror surface	300	
	$10^8$	$10^{10}$	$3 \times 10^7$	high purity, single crystal	77	Volzhenskii & Pashkovskii,
	$2 \times 10^4$	$10^5$	200		300	Ioffe & Patrina, Patrina & Ioffe
	120	$10^4$	50		450	
	1.6	4	$0.4 \times 10^3$ ohm-cm	single crystal	293	Allersma et al.
		25	ohm-cm	liquid in air	670°C	
		7		liquid in argon		
		$10^5$		high density, amorphous film	300	
		$10^6$		low density, amorphous film	300	
		$1.1 \times 10^6$		0.5-5μ thick, amorphous film	300	Kennedy et al.
		$3 \times 10^4$	ohms	P < 100 kbars	300	Minomura & Drickamer
		$10^3$		P = 100-105 kbars		
		$4 \times 10^4$		P > 105 kbars		
		$10^4$		P > 300 kbars		
Mobility		5	$\text{cm}^2/\text{V sec}$	high purity, macrocrystalline	300	King & Suber

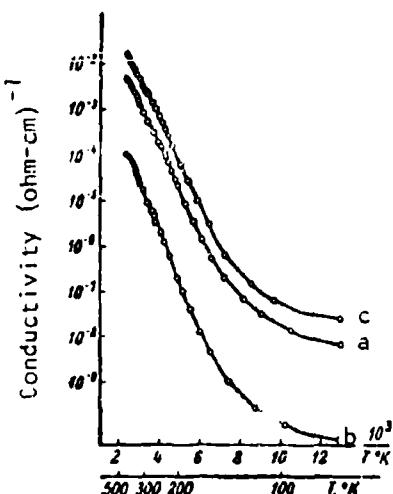
THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Mobility	a	b	c (axes)			
	$10^{-2}$	$3 \times 10^{-4}$	$5 \times 10^{-2}$	high purity, single crystal	300	Volzhenskii & Pashkovskii
	$10^{-2}$	$10^{-2}$	$10^{-1}$		440	
Energy Gap	$E_{11-c}$	$E_{11-a}$	eV	optical meas. on high purity single crystal	300	Kenny et al.
	2.34	2.36				
	2.49	2.54		single crystal, optical meas. at 0.47-0.56 $\mu$	0	Bodo & Hevesi
Temperature Coefficient	$dE_g/dT$	-6.1	-7.3	$10^{-4}$ eV/°K	293-653	Bodo & Hevesi
Seebeck Coefficient	a	b	c (axes)			
	-5.8	-6.4	$-8 \mu\text{V}/^\circ\text{K}$	high purity, single crystal,	180	Volzhenskii & Pashkovskii
	-9	-8.2	-10	max. at 250°K	250	
Magnetic Susceptibility	$x_g$	+0.4	$10^{-6}$ cgs	yellow form	300	Tourky et al.
		+1.1			100-400	Roch
	$H \perp b\text{-axis}$	$H \parallel b\text{-axis}$		single crystal plates, H=5 kOe	77-300	Khan et al.
	0.3	0.2 ( $10^{-6}$ )				
OPTICAL						
Transmission		60	%	0.8 $\mu$ thick film $\lambda = 0.52 \mu$		Sinciair et al.

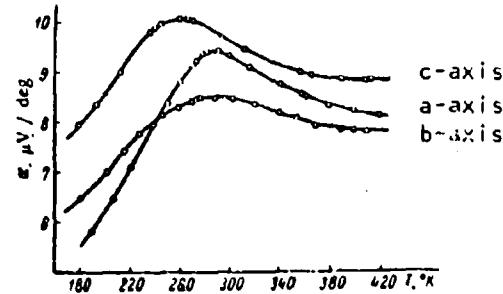
THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Refractive Index		Wavelength ( $\mu$ )				
		0.55-0.75	0.6708	0.5893		
	$n_a$	2.07	2.70	2.89	single crystal, birefringent	300
	$n_b$	1.97	2.07	2.10		Kenny et al., King & Suber
	$n_c$	2.12	2.45	2.55		

V<sub>2</sub>O<sub>5</sub> - ELECTRICAL PROPERTIES



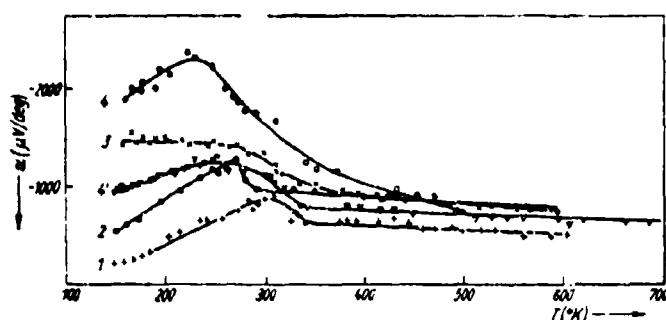
Electrical conductivity as a function of temperature in single crystal V<sub>2</sub>O<sub>5</sub> along the three crystal axes.



Thermoelectric power in single crystal V<sub>2</sub>O<sub>5</sub> grown under 5 atm. oxygen pressure. Maximum at 250°K for thermal emf along the c-axis.

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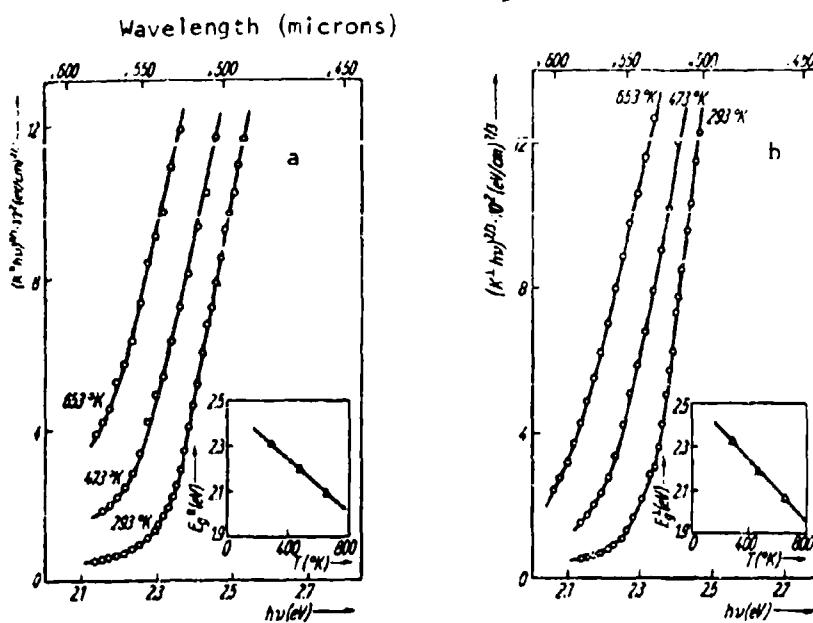
Volzhenskii & Pashkovskii,  
Ioffe & Patrina  
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Thermoelectric power as a function of temperature for V<sub>2</sub>O<sub>5</sub> single crystals.  
#4 is annealed at 800°K

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$V_2O_5$  - OPTICAL PROPERTIES

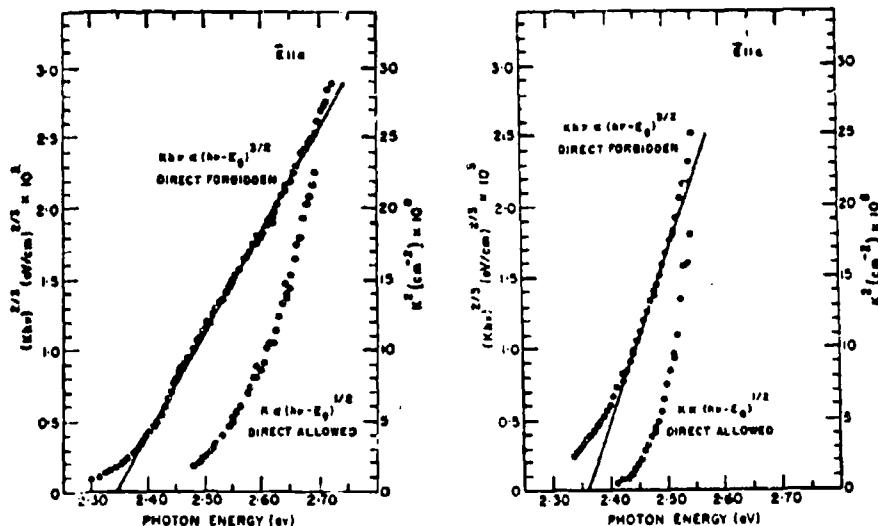


Absorption edge as a function of wavelength in single crystals of  $V_2O_5$  at three temperatures.

- a. E parallel to c-axis
- b. E normal to c-axis

Bodo & Hevesi

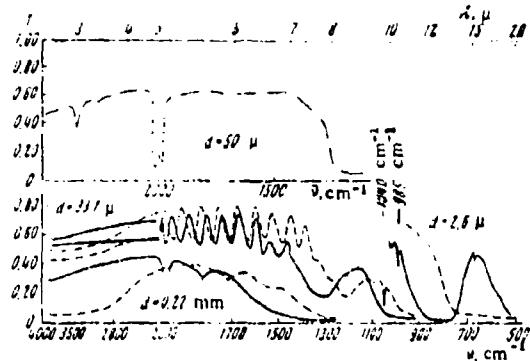
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Absorption edge as a function of wavelength in single crystals of  $V_2O_5$  at 293°K.

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$V_2O_5$  - OPTICAL PROPERTIES

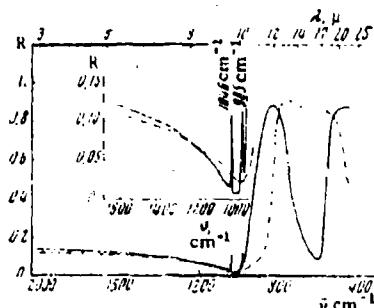


Transmission spectra of single crystals at 300°K.

----- E II a

-·--- E II b

— E II c



Reflectance spectra of single crystals;  
spectra in the narrow band region are  
shown in the insert.

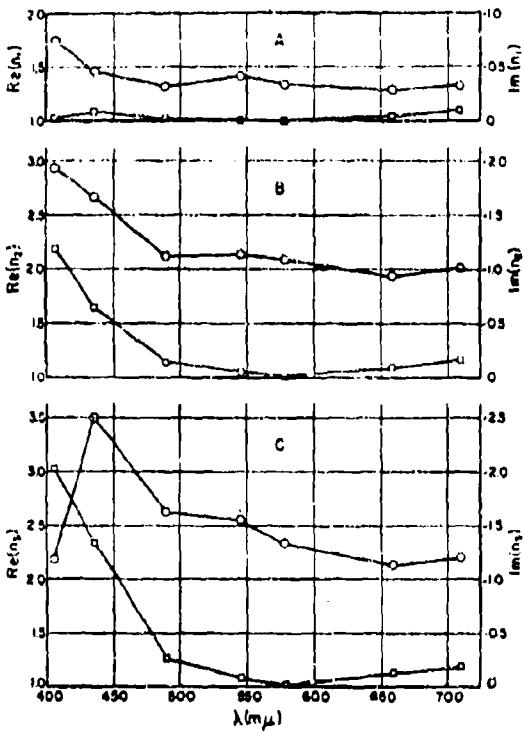
— E II a

----- E II c

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Hevesi et al.

## $V_{2}O_5$ - OPTICAL PROPERTIES



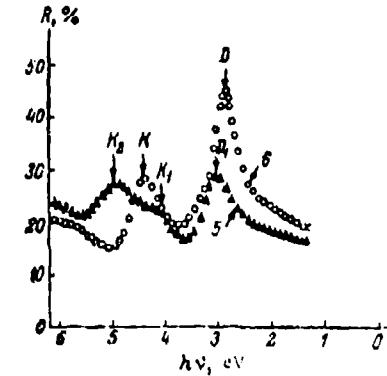
Optical constants of single crystal  $V_{2}O_5$  at 300°K (monoclinic phase)

- The three refractive indices as a function of wavelength
- Imaginary components

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Journal of the Optical  
Society of America

Transmission as a function of  
wavelength for a sputtered  
 $V_{2}O_5$  film, 0.8  $\mu$  thick.

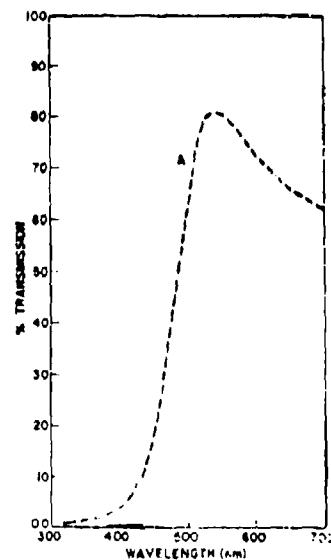
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Electrochemical Society



Reflectivity as a function of wavelength for single crystals at 300°K

5. Ell c-axis, 6. Ell a-axis

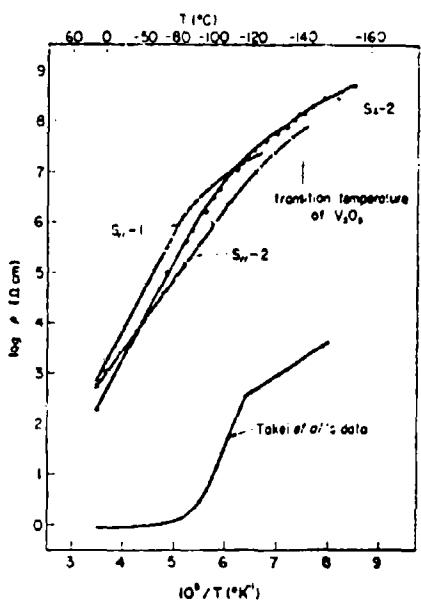
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THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		V <sub>3</sub> O <sub>5</sub>		VO <sub>1.65-1.67</sub>		Kosuge [B]
Molecular Weight		232.826				
Density		4.55	g/cm <sup>3</sup>			Donnay
Symmetry		monoclinic		Z-4		Donnay
Lattice Parameters	a <sub>0</sub>	9.835	Å			Donnay
	b <sub>0</sub>	5.031				
	c <sub>0</sub>	6.974				
	θ	109° 28'				
Electrical Resistivity		250	ohm-cm	single crystal, meas. ⊥ growth-axis, slightly anisotropic, no transition	300	Okinaka [A] et al.
		10 <sup>6</sup>			185	
		2 × 10 <sup>8</sup>			115	
		2 × 10 <sup>3</sup>		sintered	300	Kachi et al.
		2 × 10 <sup>5</sup>			185	
Seebeck Coefficient		-250	μV/°K	single crystals	300	Okinaka [A] et al.
		-400			200	
Magnetic Susceptibility	x <sub>g</sub>	24	10 <sup>-6</sup> cgs	single crystals	250	Nagasawa [B] et al.
		30			77	

$V_3O_5$  - ELECTRICAL PROPERTIES

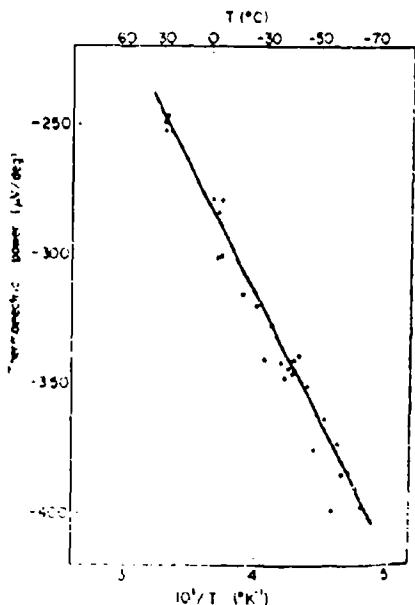


Electrical resistivity as a function of temperature for single crystal  $V_3O_5$ . Two samples were measured; from 250 to 300 $^{\circ}\text{K}$  by a four point method and below 250 $^{\circ}\text{K}$  by a two point method. Measurements were made as indicated, parallel and normal to the growth axis.

Okinaka et al.

Thermoelectric power as a function of temperature for single crystals.

Okinaka et al.



THE VANADIUM-OXYGEN SYSTEM

PHYSICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		V <sub>2</sub> O <sub>3</sub>				
Molecular Wgt.		149.88				
Density		5.05	g/cm <sup>3</sup>	monoclinic		Donnay
Color		black				Handbook
Symmetry		monoclinic				Donnay
Lattice Parameters	a <sub>0</sub>	13.88	Å	<160 °K		Donnay
	b <sub>0</sub>	4.98				
	c <sub>0</sub>	8.57				
	β	91°36'				
	V-V	2.745	Å	face (a-c plane)		Dernier &
	V-V	2.987		edge		Marezio
Symmetry		hexagonal		α-corundum		Donnay
Lattice Parameters	a <sub>0</sub>	4.948	Å			McWhan &
	c <sub>0</sub>	13.97				Rice,
	V-V	2.700		face		Nakahira et
	V-V	2.872		edge		al., Newnham
						& de Haan
Density		4.98	g/cm <sup>3</sup>	single crystal		Zhuze et al. [A]
Melting Point		2050	°C			Stringer
Specific Heat		0.165	cal/gr °K		300	TPRC,
		0.24			1700	p. 530
		0.25			1800	

THE VANADIUM-OXYGEN SYSTEM

PHYSICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Thermal Expansion		~2	$10^{-4}$ /°K	hot pressed at 1100°C	173°C	Fox
		~1	$10^{-5}$ /°K		300-800°C	
<b>ELECTRICAL PROPERTY</b>						
Dielectric Constant						
Static	$\epsilon_0$	15 ( $\pm 20\%$ )		polycrystalline at 1 MHz	53	MacMillan, p. 18
		18		$V_2O_3$ , <sub>7</sub> pressed powder,	<160	Samokhavalov
		36		$\rho_{300} = 50 \Omega\text{-cm}$ at 10 GHz		
Optical	$\epsilon_\infty$	~5		single crystal	$>T_c$	Zhuze et al. [8]
Electrical Resistivity		$1.3 \times 10^{-4}$	$\Omega\text{-cm}$	high purity, single crystal	300-170	Goodman
		$10^5$			168	
		$10^7$			115	
<b>  -c plane      -a plane</b>						
		$3 \times 10^{-4}$	$1 \times 10^{-4}$	single crystal	285	MacMillan
		$5.6 \times 10^{-4}$	$6.3 \times 10^{-4}$	single crystal	273	Feinleib & Paul
		$10^4$			150	
		$10^5$			120	
		$12 \times 10^{-4}$			500	
		21			600	
		26			700	
		29			800	
		$10^4$		amorphous, sputtered film	<170	MacKenzie
		$10^{-2}$			>170	

THE VANADIUM-OXYGEN SYSTEM

ELECTRICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES	
<b>Electrical Resistivity</b>							
Temperature $\rho(T)/\rho(0^\circ\text{C})$		$0.36+2.3 \times 10^{-3} T(\text{°K})$		single crystal	150-350	Feinleib & Paul	
Pressure Coeff.		$\frac{\partial \rho}{\partial P}$	$11-\text{c}$ $11-\text{a}$	$-4.3 - 8.8 \times 10^{-6} \Omega\text{-cm/kbar}$ $P=6 \text{ kbar}$	300		
Volume Coeff.			$11-\text{a}$	$42$ $20$	$P=1 \text{ bar}$ $P=25 \text{ kbar}$	300	McWhan & Rice
Transition Temperature	$T_c$	$172 \pm 4$	°K	high purity, single crystal		Goodman, McWhan & Rice, Morin	
Pressure Coeff.	$dT_c/dP$	-4.1	°K/kbar	$P=15 \text{ kbar}$ , single crystal	150	Austin	
		-3.78		$P=6 \text{ kbar}$		Feinleib & Paul	
		-3.1		$P=160 \text{ kbar}$	77-500	Minomura & Nagasaki	
Stress Coeff.	$dT_c/dS$	<u>a    b    c (axes)</u> $-6.8 - 4.1 - 0.5$	°K/kbar	single crystal	300	Feinleib & Paul	
<b>Mobility</b>							
Hole	$\mu_p$	0.55 0.40	$\text{cm}^2/\text{V sec}$	single crystal	200 300	Zhuze et al. [A]	
Temperature Coeff.			$T^{-0.7}$				
Hole	$\mu_p$	0.6 0.2			300 700	Austin & Turner	
Hole	$\mu_p$	$1.5 \times 10^{-4}$		single crystal	125	MacMillan	

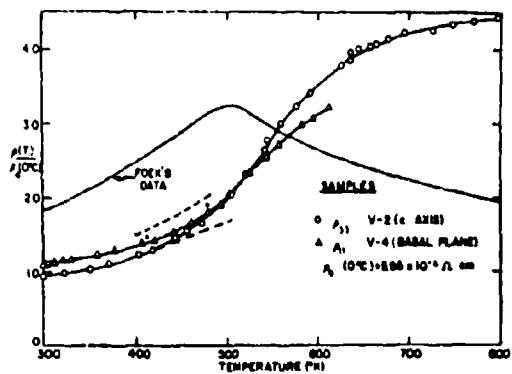
## THE VANADIUM-OXYGEN SYSTEM

ELECTRICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Effective Mass	$m^*$	45-50	$m_0$	single crystal	$>T_c$	Feinleib & Paul, Adler & Feinleib
		11		optical meas. on single crystal	$>T_c$	Zhuze et al. [B]
Mean Free Path		2	$\text{\AA}$			Feinleib & Paul, Adler & Feinleib
Energy Gap		0.1	eV	optical meas.	77	Feinleib & Paul, Adler & Feinleib,
		0.12-0.18		electrical meas.	150-170	Barker & Remeika
Pressure Coeff.	$dE_g / dP$	-4.4	$10^{-6}$ eV/bar	single crystal		Feinleib & Paul, Austin
Seebeck Coeff.	$Q_{  }$	10.5	μV/°K	single crystal	285	MacMillan
	$Q_{\perp}$	3.2				
	$Q$	+350 -400		p-type n-type	100 100	
	$Q_{  }$	~12 <-5			170-500 100-150	Austin & Turner
Magnetic Susceptibility	$x_g$	$\sim 10^{-7}$	cgs	single crystal	>170	MacMillan
		3.8	$10^{-6}$ cgs	pressed powder	90	Bogdanova & Loginov
		6.4			293	
	$x_{  } \quad x_{\perp}$	$6.9 \quad 5.9$ $11.2 \quad 12.2$	$10^{-6}$ cgs	single crystal	<170 >170	Carr & Foner, Nakahira et al.
		12.42 12.58 11.24 10.88				
				single crystal	300	Arnold & Mires, Gossard & Menth

THE VANADIUM-OXYGEN SYSTEM

OPTICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Wavelength ( $\lambda$ )						
Transmission		0 maximum	0.2-20		300 77	Feinleib & Paul, Barker & Remeika
Refractive Index		1.84 1.67 1.95 6.8 8.8	0.4 1.0 2.0 10.0 20.0	single crystal	300	Zhuze et al. [B]

$V_2O_3$



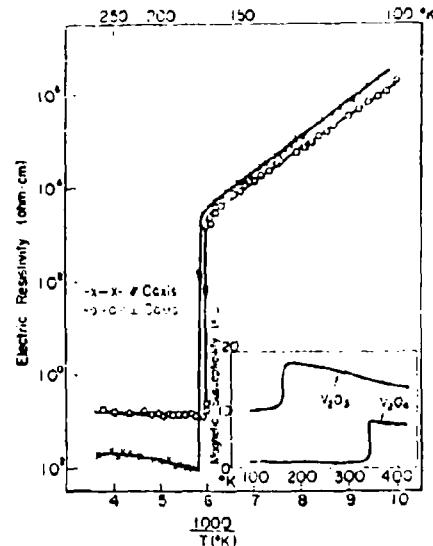
Electrical resistivity as a function of temperature to 800°K for single crystals.

$\rho_{33}$  measured along c-axis

$\rho_{11}$  measured in basal plane

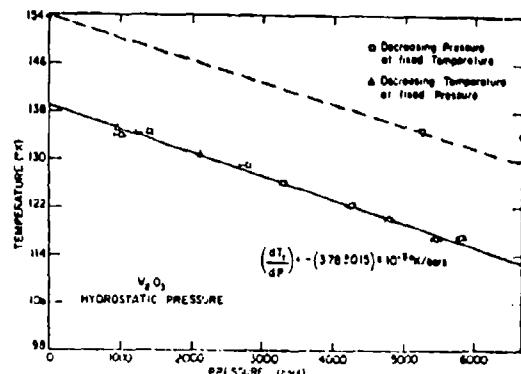
Foex's data on sintered bars are included.

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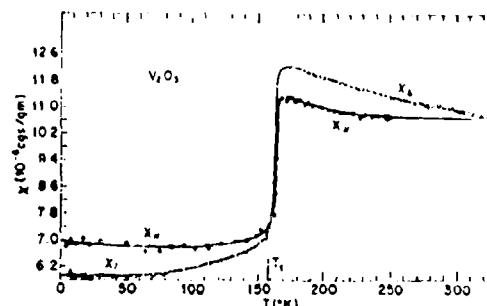
Resistivity as a function of temperature in single crystals.

Kosuge, A



Transition temperatures as a function of hydrostatic pressure in single crystals.

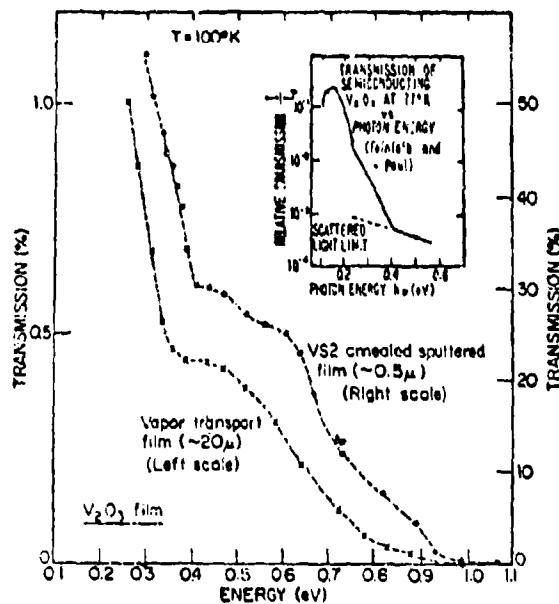
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Magnetic susceptibility as a function of temperature in single crystals, parallel and normal to the basal plane.

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## $V_2O_3$ - OPTICAL PROPERTIES

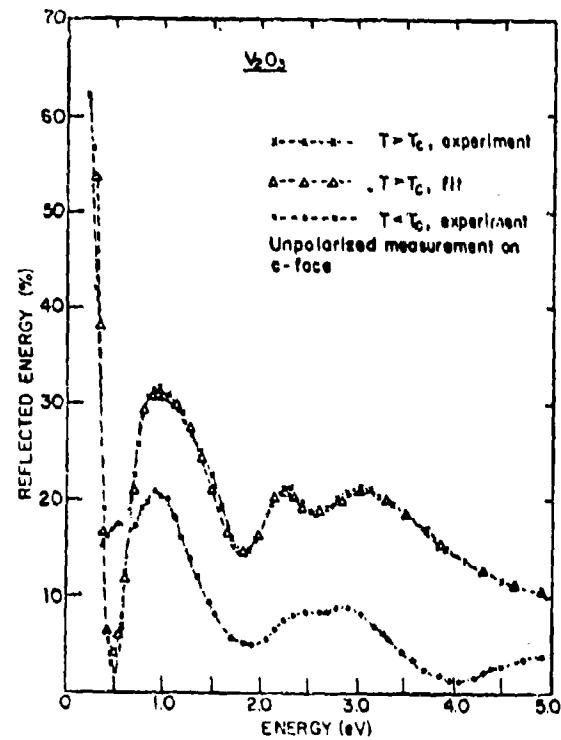


Low temperature transmission of a single crystal, epitaxial  $V_2O_3$  film grown by vapour transport and of an annealed, sputtered film. Data from these two films are compared with transmission from a single crystal as reported by Feinleib and Paul.

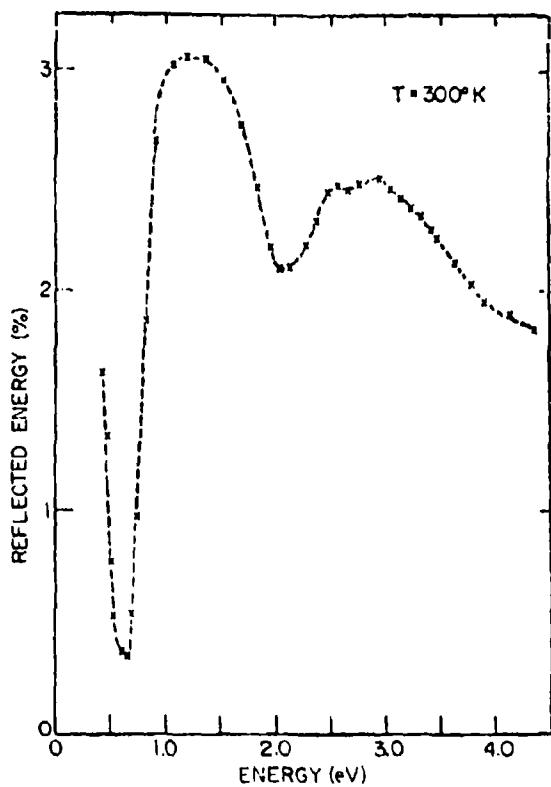
Fan & Paul

Reflectivity of a single  $V_2O_3$  crystal, above and below the transition temperature.

Fan & Paul



$V_2O_3$  - FILMS



Reflectivity as a function of wavelength  
for a single crystal, epitaxial film.  
The substrate is single crystal alumina  
with the c-axis normal or parallel to  
the substrate plane.  
 $T_1 = 800^\circ\text{C}$ ,  $T_2 = 60^\circ\text{C}$

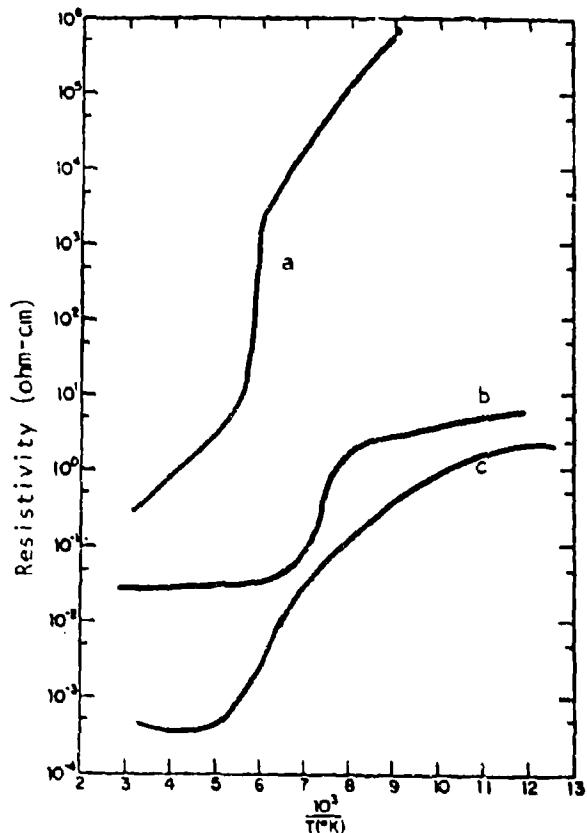
Measurements in the infrared and visible  
are made above the transition temperature.

Fan & Paul

Electrical resistivity as a  
function of temperature for  
 $V_2O_3$  films.

- a. sputtered, polycrystalline film,  
about  $0.55\mu$  thick, alumina sub-  
strate, annealed at  $600^\circ\text{C}$
- c. similar film but showing great  
difference in resistivity
- b. single crystal, epitaxial film,  
grown by vapour transport on  
alumina substrate

Fan & Paul

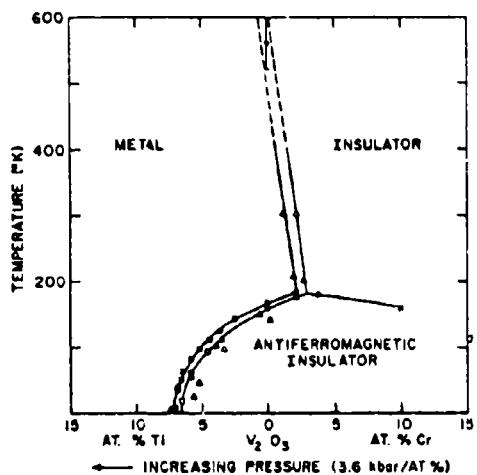


Crystal Structure, Transition Temperature and Conductivity in  $V_{1-x}Ti_xO_2$

Composition x	Monoclinic (25°C)				Rutile		Transition Temp. (°C)	Conductivity at 40°C (ohm-cm) <sup>-1</sup>
	$a_o$	$b_o$	$c_o$	$\beta$	$a_o$	$c_o$		
0.00	5.744	4.520	5.376	122.6	4.559	2.801	69	0.8
0.02	5.729	4.530	5.364	122.3	-	-	65	1.2
0.05	5.727	4.560	5.390	122.5	4.545	2.844	63	-
0.10	5.716	4.499	5.424	122.0	4.537	2.868	60	5.8
0.20	5.704	4.490	5.448	121.3	4.539	2.891	58	4.7
0.40	4.833	4.380	5.530	97.9	4.546	2.894	48	0.3

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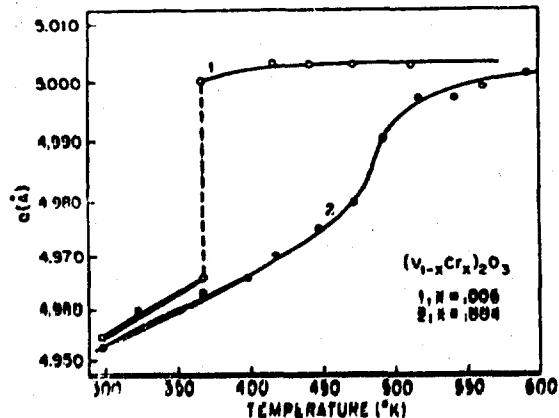
Rao et al.



Generalized phase diagram of transition temperature as a function of both pressure and at. % of chromium and titanium in  $V_2O_3$

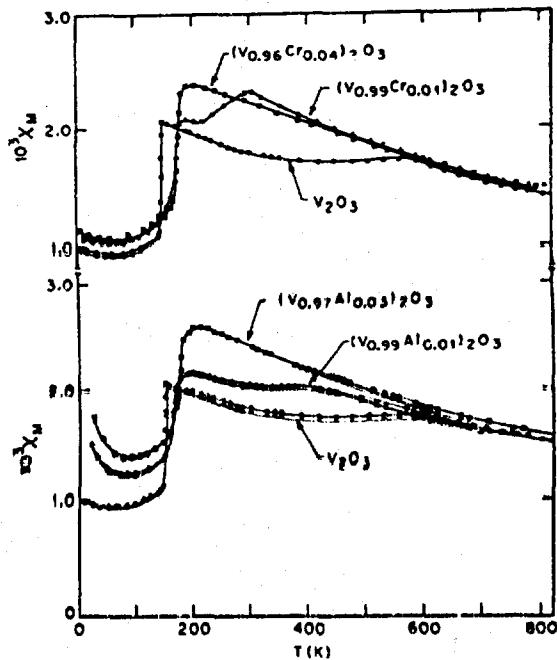
- mixed oxides at 1 atm.
- □  $V_2O_3$  on increasing and decreasing pressures, resp.
- ▲ △  $(V_{0.96}Cr_{0.04})_2O_3$  for increasing and decreasing pressure

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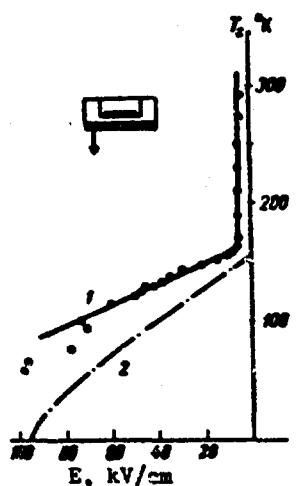
Lattice parameters as a function of temperature for two chromium-doped  $V_2O_3$  crystals.

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Magnetic susceptibility as a function of temperature for  $V_2O_3$  and for chromium and aluminum containing  $V_2O_3$ . The undoped and chromium containing  $V_2O_3$  were single crystals and the susceptibility was measured parallel to the c-axis. The aluminum containing samples are ceramic powder aggregates.

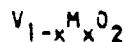
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Transition temperature as a function of electrical field in sintered  $(V_{0.91}Cr_{0.09})_2O_3$ . The electrical field shifts the transition temperature similarly to the shift by hydrostatic pressure.

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INITIAL RATE OF CHANGE OF UPPER TRANSITION TEMPERATURE  
WITH COMPOSITION ( $dT_t/dx$ ) FOR THE SUBSTITUTIONAL COMPOUNDS



[Critical compositions  $x_1$  and  $x_2$  indicate phase changes at 300°K. Room-temperature structures within the regions  $x_1 < x < x_2$  and  $x > x_2$  are also indicated, where mono. refers to the monoclinic (P2/c) phase and ortho. to the orthorhombic (probable space group F222) phase.]

M	$dT_t/dx$ [°K/at % M]	$x_1$	$x_2$	$x_1 < x < x_2$	$x > x_2$
$Cr^{3+}$	$\sim +3$	0.01	0.20	ortho.	(2φ)*
$Fe^{3+}$	+3	0.01	0.125	ortho.	two-phase
$Ga^{3+}$	+6.5	0.005	0.02	ortho.	two-phase
$Al^{3+}$	+9.0	0.005	0.045	ortho.	two-phase
$Ti^{4+}$	-0.5 to -0.7	0.2	0.2 to 0.25	ortho.	rutile and (2φ)*
$Re^{4+}$	$\sim -4$	0.07		rutile	
$Ir^{4+}$	$\sim -4$	0.04	0.5	rutile	two-phase
$Os^{4+}$	-7	0.03	0.1	rutile	two-phase
$Ru^{4+}$	-10	0.025	0.75	rutile	two-phase
$Ge^{4+}$	+5				
$Nb^{5+}$	-7.8	0.05	0.9	rutile	$NbO_2$
$Ta^{5+}$	-5 to -10	0.02	0.5	rutile	two-phase
$Mo^{6+}$	-5 to -10	0.03	0.55	rutile $x = 1.0$	(2φ)* mono.
$W^{6+}$	-28	0.013	0.68	rutile	ortho.
ordered trirutile phase about $x = 0.33$ ; $0.78 < x < 0.8$ (2φ')* phase; $0.85 < x < 1$ mono.					
* The 2φ phase is a distorted rutile structure with orthorhombic symmetry, and the 2φ' phase is similar but with monoclinic symmetry.					

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